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HETEROGENEOUS CHEMISTRY RELATED TO ANTARCTIC OZONE DEPLETION: REACTION OF $ClONO_2$ AND N_2O_5 ON ICE SURFACES

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Laboratory studies of heterogeneous reactions of possible importance for Antarctic ozone depletion have been performed. In particular, the reactions of chlorine nitrate ($ClONO_2$) and dinitrogen pentoxide (N_2O_5) have been investigated on ice and HCl/ice surfaces. Reactions 1 and 2, proposed to

$$ClONO_2 + H_2O \rightarrow HNO_3 + HOCl \qquad (1)$$

$$ClONO_2 + HCl \rightarrow HNO_3 + Cl_2 \qquad (2)$$

occur on the surfaces of polar stratospheric clouds (PSCs) over Antarctica,[1] transform the stable chlorine reservoir species ($ClONO_2$ and HCl) into photochemically active chlorine in the form of HOCl and Cl_2. Condensation of HNO_3 in the above reactions removes odd nitrogen from the stratosphere, a requirement in nearly all models of Antarctic ozone depletion.[1-4]

Reactions 3 and 4 may also be important for Antarctic ozone depletion.

$$N_2O_5 + H_2O \rightarrow 2\ HNO_3 \qquad (3)$$

$$N_2O_5 + HCl \rightarrow HNO_3 + ClNO_2 \qquad (4)$$

Like the reactions of chlorine nitrate, these reactions deplete odd nitrogen through HNO_3 condensation. In addition, reaction 4 converts a stable chlorine reservoir species (HCl) into photochemically active chlorine ($ClNO_2$). Reactions 1 - 4 were studied with a modified version of a Knudsen cell flow reactor.[5]

Heterogeneous Reactions of Chlorine Nitrate on Ice

Chlorine nitrate reacted readily with H_2O and HCl on ice surfaces at 185 K. Upon exposure of an ice surface to $ClONO_2$, gas phase HOCl was detected (reaction 1). Formation of gaseous Cl_2O was also observed. As discussed in [6], Cl_2O is thought to be formed in a secondary reaction. The other product of reaction 1, HNO_3, is not observed in the gas phase. However, when the surface is slowly warmed, HNO_3 is detected in thermal desorption spectrometry (TDS). Thus reaction 1 on ice produces gas phase HOCl and condensed phase HNO_3. The sticking coefficient for $ClONO_2$ on ice measured using m/e 46 is determined as 0.009 ± 0.002 (1 standard deviation).

The reaction of $ClONO_2$ with HCl on ice, reaction 2, may be especially important in the Antarctic stratosphere because it converts two chlorine reservoir species into photochemically active Cl_2. We and others[7,8] have observed this reaction to proceed readily. This reaction was studied on a surface prepared by co-condensing a 7:1 ratio of H_2O:HCl onto a wax-coated copper block at 185 K. When $ClONO_2$ was introduced into the Knudsen cell containing this surface, gas phase Cl_2 was formed. Cl_2 does not stick to, or react with, ice at 185 K. The reaction of $ClONO_2$ on HCl/ice proceeded until at least 95% of the total deposited HCl was depleted, indicating rapid diffusion of HCl in ice.[7] As was the case for reaction 1, HNO_3 formed via reaction 2 was observed in TDS after the reaction by slowly warming the sample.

Heterogeneous Reactions of Dinitrogen Pentoxide on Ice

Dinitrogen pentoxide reacted readily with ice and HCl/ice at 185 K. When N_2O_5 was exposed to ice at this temperature, loss of N_2O_5 was indicated by a large decrease in the m/e 46 mass spectrometer signal. No new mass signals were observed in this reaction. Assuming that only N_2O_5 contributes to m/e 46, the sticking coefficient for N_2O_5 on ice is determined as 0.001 (± 50% in 10 determinations). To the extent that other species contribute to m/e 46, this should be considered a lower limit to the true value.

The product of reaction 3, HNO_3, was observed after the reaction in TDS. Figure 1a displays the nitric acid TDS signal after reaction of N_2O_5 on ice for 15 minutes at 185 K. Two desorption peaks are observed. Studies indicate that the lower temperature peak is due to overlayers of HNO_3, and the higher temperature peak is due to hydrates of HNO_3.[9] Figure 1b displays the HNO_3 signal after exposure of N_2O_5 at the same pressure to halocarbon wax-coated copper for 15 minutes at 185 K. The small signal in this figure is thought to be due to impurity HNO_3 in the N_2O_5. It can be seen that the HNO_3 produced from reaction 3 is much more abundant than that due to impurity.

The reaction of N_2O_5 with HCl was studied on a cold wax-coated copper surface and on ice. The Knudsen cell effluent for the reaction of N_2O_5 with HCl on waxed copper at 185 K is shown in Figure 2a. For comparison, the mass spectrum of $ClNO_2$ is shown in Figure 2b. The similarity in these two spectra suggests that $ClNO_2$ is a gas phase product of reaction 4. Similar spectra were obtained for the reaction of N_2O_5 on HCl/ice surfaces at 185 K. $ClNO_2$ did not stick to, or react with, ice at 185 K. As was the case for the reaction of $ClONO_2$ with HCl, reaction 4 proceeded until essentially all of the HCl in the ice was depleted. HNO_3 was observed in the ice after reaction using TDS.

Heterogeneous Reactions on Acidic Surfaces

As discussed above, reactions 1 - 4 proceed readily on ice surfaces at 185 K. Reaction 1 has also been studied on several acidic surfaces that may be more representative of the PSCs over Antarctica. It was found that reaction 1 occurs on only certain nitric acid/ice surfaces at 185 K. Of surfaces prepared by co-condensation of 1:2, 2:1, and 4.5:1 mixtures of $H_2O:HNO_3$, only the latter one promoted reaction 1.[6] These results suggest a critical amount of water is needed for the reaction to proceed.

Reaction 1 was also studied on sulfuric acid surfaces. It was found that this reaction proceeded readily on 95% H_2SO_4 at room temperature.[10] This reaction did not, however, occur on 95% H_2SO_4 at 185 K.[6] We are currently investigating reactions 1 and 2 on low temperature sulfuric acid surfaces of varying composition (65 - 85% H_2SO_4). The effects of temperature and acid concentration on the reaction efficiencies will be discussed.

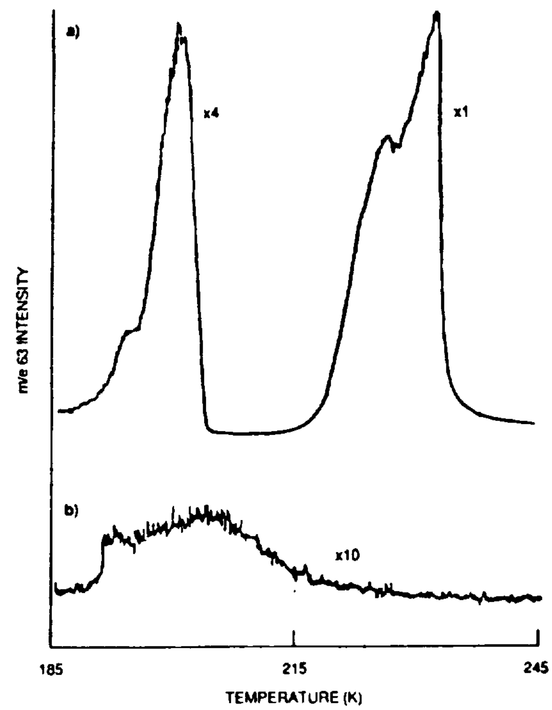

Figure 1 TDS scans of HNO_3 after a) exposure of ice to N_2O_5 (P = 1 mTorr) for 15 minutes and b) exposure of cold wax-coated copper to N_2O_5 at the same pressure for the same time.

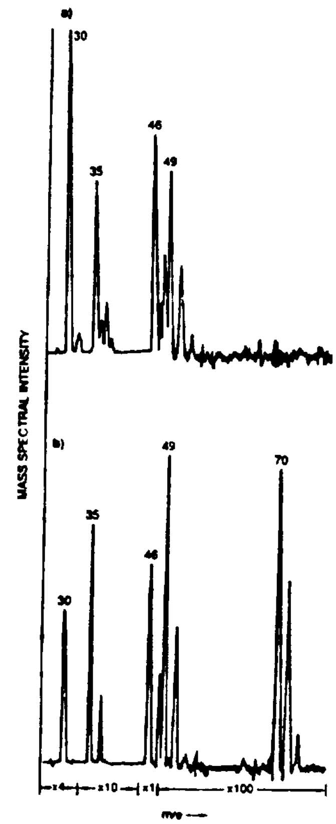

Figure 2 Mass scans for the Knudsen cell effluent for a) the reaction of N_2O_5 with HCl on wax-coated copper at 185 K and b) gas phase $ClNO_2$ with a 5% Cl_2 impurity.

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